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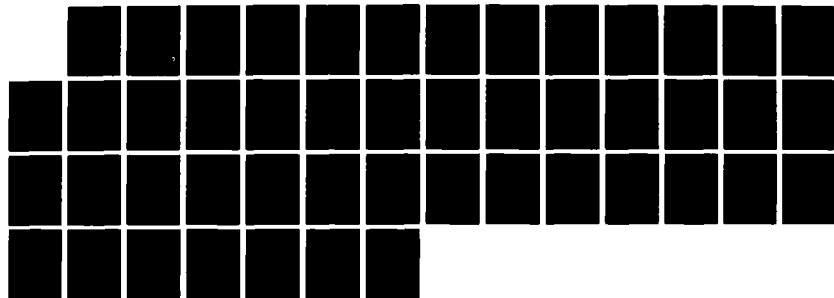
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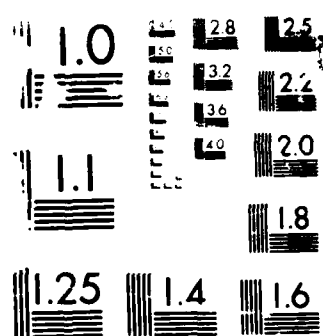
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Semiempirical Study of Polyatomic Rare Gas Halides: Application  
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by

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Semiempirical study of polyatomic rare gas  
halides: Application to the  $\text{Xe}_n\text{Cl}$  systems

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Abstract

In order to calculate different electronic states in polyatomic rare gas-halogen systems, including ionic states with charge transfer, a semiempirical diatomics-in-ionic-systems (DIIS) method is presented. In this method the Hamiltonian matrix elements are expressed in terms of diatomic potentials, except for those which are responsible for coupling between the ionic and neutral states. The coupling matrix elements are determined by fitting the diatomic transition moments. Calculations are performed for  $\text{Xe}_2\text{Cl}$ ,  $\text{Xe}_3\text{Cl}$  and  $\text{Xe}_{12}\text{Cl}$ . The results reveal at least three quasistable ionic  $\text{Xe}_2^+\text{Cl}^-$  molecules. Such molecules can attract more Xe atoms, which are binded mainly by polarization forces.



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## I. Introduction

Interest in rare gas-halogen systems has been increasing due to their spectroscopic, and in particular lasing, properties.<sup>1-12</sup> The lasing properties are associated with the formation of quasistable ionic molecules  $R^+X^-$  and  $R_2^+X^-$ , where R and X are the rare gas and halogen atoms, respectively. These ionic molecules are obtained in rare gas-halogen gas mixtures either by electron impact<sup>1-4,7,8</sup> or by optical, most often laser, irradiation.<sup>5,9,11,12</sup> Recently the ionic rare gas-halogen molecules  $Xe_2^+Cl^-$  were detected also in rare gas solids doped by  $Cl_2$  and  $HCl$ .<sup>13,14</sup> Rare gas-halogen systems are of interest not only for the configurations where the quasistable ionic  $R^+X^-$  and  $R_2^+X^-$  molecules are formed, but also for configurations of van der Waals  $RX$ ,  $RX_2$  or  $RXH$  complexes.<sup>15-19</sup>

The theoretical consideration of the rare gas-halogen systems involves a knowledge of potential curves and potential energy surfaces (PES). The calculation of these PES is the aim of the present paper. For the sake of generalization, we shall consider here arbitrary  $R_nX$  systems where n may be larger than 2 and consequently the number of atoms larger than 3. Although the  $RX$  and  $R_2X$  systems have been mostly the subject of study, the  $R_nX$  systems with  $n > 2$  can also be of interest due to the possibility of the formation of cluster-like molecules or large van der Waals complexes. The  $R_n^+X^-$  ( $n > 2$ ) excited systems can also be formed in rare gas solids doped by halogen molecules.<sup>20</sup>

In the case of diatomic  $RX$  ( $n = 1$ ) systems some of the potential curves for different electronic states are well known from ab initio calculations.<sup>21-23</sup> The  $RX$  potential curves, mostly for the ground state, were studied also by applying model approach<sup>24</sup> and by using experimental data.<sup>4,15,26</sup> The information concerning the triatomic  $R_2X$  systems, not to

mention the  $R_nX$  systems for  $n > 2$ , is much more scarce. The experimental data of the  $R_2X$  systems are limited mainly to the transition energies.<sup>7,9,11,12</sup> The all-electron ab initio calculations were performed for the  $Ar_2F$  and  $Kr_2F$  systems only.<sup>27</sup> The ab initio calculation of the  $Xe_2Cl$  system which contains many more electrons was performed by using a simplified model.<sup>28</sup> The  $R_2X$  systems were also calculated semiempirically by using the diatomics-in-molecules (DIM) method.<sup>29,30</sup>

The advantages of the semiempirical approach in the PES calculations of polyatomic systems containing a large number of electrons are well known. In particular, the DIM method is often used in the PES calculations.<sup>37</sup> Unfortunately, in the case where ionic states are involved, the application of the DIM method becomes much more complicated if the coupling between the neutral and ionic states is taken into account.<sup>32</sup> The difficulties arise largely due to the "zero overlap of atomic orbitals" approximation which is usually used in the DIM method. According to this approximation, the overlap between atomic orbitals belonging to different atoms is neglected. Consequently the off-diagonal matrix elements between any electronic configurations with different numbers of electrons on the same atom, like the neutral and ionic states, are equal to zero, such that the states are uncoupled. This shortcoming of the usual DIM method can be overcome by introducing additional assumptions and new parameters.<sup>32-34</sup> However, such an approach increases the complexity of the calculation and makes the results more arbitrary. In DIM calculations of the  $R_2X$  systems,<sup>29,30</sup> the usual version of the method was used with the off-diagonal matrix elements between neutral and ionic states equal to zero and the independent consideration of the  $R_2X$  and  $R_2X^{\pm}$  states.

The influence of the coupling between the neutral and ionic states of the  $R_nX$  systems is not quite clear. This problem was studied only in the connection with ab initio calculations of the XeX diatomic systems.<sup>22</sup> According to this study, the coupling is of the order of 10% for the equilibrium XeX van der Waals distance and decreases slowly as the interatomic distance increases. It is difficult to estimate the influence of the coupling on different properties of the RX systems, although it obviously reduces size of the van der Waals RX molecule. For example, the van der Waals radii of the Xe and Cl atoms are 2.2 Å and 7.8 Å,<sup>35</sup> respectively, and while the XeCl van der Waals distance is expected to be 4.0 Å, in reality it is only 3.23 Å.<sup>26</sup> Because the coupling may be different for different rare gas-halogen systems, the use of diatomic RX potential curves in the semiempirical calculations of polyatomic systems (DIM, for example) may lead to confusing results. Thus, the coupling and consequently the interaction are expected to be small in the case of a  $RX_2$  van der Waals complex due, partly, to lower electron affinity of the  $X_2$  molecule compared to the X atom,<sup>20</sup> which is confirmed by the spectroscopic properties of  $X_2$  molecules trapped in a rare gas matrix.<sup>36</sup> However, neglecting the change in the coupling and using the empirical RX interaction in the DIM calculation of the van der Waals  $RX_2$  molecule, one would obtain the  $RX_2$  interaction as strong, roughly, as in the R-X case, in contradiction with the experiment. The coupling between neutral and ionic states must be taken into account if one wants to calculate the off-diagonal (transition) dipole moments.

We shall present in this paper a semiempirical method which is designed for a calculation of rare gas-halogen systems  $R_nX$  consisting of an arbitrary number of rare gas atoms and one halogen atom. Introducing some



modifications, the method can be extended to  $R_nHX$  systems. The method takes into account in a straightforward way the coupling between the neutral  $R_nX$  and the ionic  $R_n^+X^-$  configurations, as well as the positive charge delocalization in the ionic  $R_n^+X^-$  states. The method makes use of diatomic potentials as initial data for a calculation, but in a different way than the DIM method. A main feature of the method is the consideration of the systems with ionic states, and hence we call it the "diatomics-in-ionic-systems" (DIIS) method.

The spin-orbit coupling in the Cl atom and  $Xe^+$  ion will be not taken into account directly. The shift of energy levels resulting from this coupling can always be incorporated indirectly by using proper empirical or ab initio potentials. The main disadvantage of the neglect of spin-orbit coupling is the loss of some of the excited states. The direct inclusion of spin-orbit coupling does not present theoretical obstacles. However, it would make the Hamiltonian matrix elements much more complicated and would increase significantly the order of the matrix. The latter is of primary concern for large systems, like rare gas solids with halogens.<sup>20</sup>

The theoretical consideration of the DIIS method is given in Section II. Section III presents the equations for the diatomic terms which determine the matrix elements of the method. The diatomic terms for the  $Xe_nCl$  systems are given in Section IV. Section V deals with the calculation of the  $Xe_nCl$  systems, namely  $Xe_2Cl$ ,  $Xe_3Cl$  and  $Xe_{12}Cl$ , and Section VI is the Conclusion.

## II. Diatomics-in-ionic-systems method

A polyatomic rare gas-halogen system  $R_nX$  will be presented here as  $R_1R_2\ldots R_{J-1}X_J$  ( $J = n + 1$ ), where the  $R_i$  atoms have a closed shell in the neutral state and P symmetry shell in the ionized state  $R_i^+$ , whereas the  $X_J$

atom has a P symmetry shell in the neutral state and a closed shell when becoming the negative ion  $X_J^-$ . The  $R_i$  atoms need not be just the rare gas atoms but also H atoms, with the difference that in the ionized state  $H^+$  they are also spherically symmetric. The systems with H atoms can be treated as a particular case which we shall not consider separately, suggesting that all  $R_i^+$  ions have a P symmetry shell.

The wave function of the polyatomic system in a fixed electronic configuration will be presented here as an antisymmetrized product of atomic group functions,<sup>37</sup> which are assumed to be exact many-electronic wave functions of individual atoms,

$$\phi_{m_1 \dots m_J} = \hat{A} \prod_i^J \chi_{im_i}, \quad (1)$$

where  $\hat{A}$  is the operator which antisymmetrized electrons belonging to different group functions  $\chi_{im_i}$  and  $m_i$  are the atomic state indexes. The atomic group functions in the polyatomic wave function (1) are not orthogonal one to another which makes the energy expression very complicated.<sup>38,39</sup> The consideration is significantly simplified by using the zero overlap of atomic orbitals (ZOA) approximation which is very common in semiempirical methods, in particular in the DIM method.<sup>31</sup> The ZOA approximation allows one to omit the antisymmetrization operator  $\hat{A}$ , thus rendering the polyatomic wave function as a simple product of atomic group functions. The mistake arising from the neglect of the overlap is proportional to the square of the interatomic overlap integrals<sup>39</sup> and has been shown to be small, at least in DIM calculations.<sup>40</sup>

In the accepted approximations, the wave function of a neutral  $R_1 R_2 \dots R_{J-1} X_J$  electronic configuration is equal to the product of S

symmetrical (closed shell)  $\chi_i^{(0)}$  group functions of the  $R_i$  atoms and the P symmetrical  $\chi_{Jm}^{(0)}$  group function of the  $X_J$  (halogen) atom,

$$\Phi_{Jm} = \prod_i^{J-1} \chi_i^{(0)} \chi_{Jm}^{(0)}, \quad m = 1, 2, 3 \quad (2)$$

where the index  $m$  indicates the orientation of the  $\chi_{Jm}^{(0)}$  group function along the  $x, y, z$ -axes. In an ionic state, one of the  $J-1$  rare gas atoms ( $R_i^+$ ) has a positive charge and is distinguished by its  $\chi_{im}^{(+)}$  group function orientation, whereas the  $\chi_J^{(-)}$  group function of the halogen ion  $X_J^-$  has S symmetry,

$$\Phi_{im} = \prod_j^{J-1} \chi_j^{(0)} \chi_{im}^{(+)} \chi_J^{(-)}, \quad i=1, 2, \dots, J-1; m=1, 2, 3; j \neq i. \quad (3)$$

The upper indexes (0), (+) and (-) indicate in Eqs. (2)-(3) and below the charge of an atom. It is important to emphasize that Eqs. (1)-(3) do not necessarily imply the one-electron approximation, since the group functions are arbitrary and can include correlation between electrons belonging to the same atom. Using the group functions product, we neglect only the interatomic correlation which describes, in particular, the van der Waals attraction. However, in the framework of the semiempirical approach, the van der Waals interaction can be taken into account indirectly by using empirical diatomic potentials.

The three functions [Eq.(2)] of the neutral configurations and the  $3(J-1)$  functions [Eq.(3)] of the ionic configurations form the polyatomic basis set. The linear combination of these functions forms the wave function of the system

$$\Phi = \sum_{i=1}^J \sum_{m=1}^3 c_{im} \Phi_{im}. \quad (4)$$

The energy levels of this wave function are obtained now in the usual way by forming the Hamiltonian matrix of order  $3J \times 3J$ , where  $J$  is the number of atoms in the system.

Due to the lack of interatomic electron permutations in the polyatomic functions of Eqs.(2) and (3), the Hamiltonian of the system can be partitioned into atomic and interatomic terms. This partitioning depends on the representation of the polyatomic wave function and changes from one matrix element to another. The Hamiltonian which is used for the evolution of the matrix elements for the neutral states has the form

$$\hat{H} = \sum_j^{J-1} \hat{h}_j(v_j) + \sum_{j_1}^{J-2} \sum_{j_2(>j_1)}^{J-1} h_{j_1 j_2}(v_{j_1} + v_{j_2}) + \hat{h}_J(v_J) + \sum_j^{J-1} h_{jJ}(v_j + v_J), \quad (5)$$

where the  $\hat{h}_j$  and  $\hat{h}_J$  terms with one index include all energy operators of the electrons belonging to one atom, the  $h_{j_1 j_2}$  and  $h_{jJ}$  terms with two indexes include the interactions between electrons and nuclei belonging to different atoms, and  $v_j$  indicates the number of electrons in atom  $j$ . We will present the energy of the system relative to the energy of separated on infinity atoms

$$E_\infty = \sum_j^{J-1} E_j^{(0)} + E_J^{(0)}, \quad (6)$$

where  $E_j^{(0)}$  and  $E_J^{(0)}$  are the energies of the rare gas and halogen atoms, respectively. Using the expressions (2), (5) and (6), one obtains the following expression for the diagonal matrix elements of the neutral states:

$$H_{Jm, Jm} = \int d\nu \phi_{Jm} \hat{H} \phi_{Jm} = \sum_{j_1}^{J-2} \sum_{j_2(>j_1)}^{J-1} U_{j_1, j_2}^{(00)} + \sum_j^{J-1} U_{j, Jm}^{(00)}, \quad m=1, 2, 3. \quad (7)$$

In Eq. (7),  $U_{j_1, j_2}^{(00)}$  and  $U_{j, Jm}^{(00)}$  are the potentials of the interaction between two rare gas atoms and between a rare gas atom and a halogen atom, respectively:

$$U_{j_1, j_2}^{(00)} = \int dv [x_{j_1}^{(0)}]^2 h_{j_1 j_2} [x_{j_2}^{(0)}]^2, \quad (8)$$

$$U_{j, Jm}^{(00)} = \int dv [x_j^{(0)}]^2 h_{jJ} [x_{Jm}^{(0)}]^2. \quad (8')$$

In the expression for the off-diagonal matrix elements of the neutral states, all integrals with one-atom operators  $\hat{h}_j$  and  $\hat{h}_J$  and with the interatomic terms  $h_{j_1 j_2}$  vanish either due to the difference in the symmetry of functions with different  $m$  or due to the ZOA0 approximation. Only the  $h_{jJ}$  terms give a non-zero contribution,

$$H_{Jm_1, Jm_2} = \int dv \phi_{Jm_1} \hat{H} \phi_{Jm_2} = \sum_j^{J-1} \int dv [x_j^{(0)}]^2 h_{jJ} x_{Jm_1}^{(0)} x_{Jm_2}^{(0)}. \quad (9)$$

Let us consider now the diagonal matrix elements for the ionic states [Eq.(3)]. The Hamiltonian for the  $\phi_{im}$  function which describes the state with a positive charge on the  $i$ -th rare gas atom and a negative charge on the  $J$ -th (halogen) atom has the form

$$\begin{aligned} \hat{H} = & \sum_j^{J-1} \hat{h}_j(v_j) + \sum_{j_1}^{J-2} \sum_{j_2(>j_1)}^{J-1} h_{j_1 j_2}(v_{j_1} + v_{j_2}) + \hat{h}_i(v_i - 1) + \sum_j^{J-1} h_{ij}(v_i - 1 + v_j) + \\ & \hat{h}_J(v_J + 1) + \sum_j^{J-1} h_{jJ}(v_j + v_J + 1) + h_{iJ}(v_i + v_J), \quad j, j_1, j_2 \neq i. \end{aligned} \quad (10)$$

This form includes terms which are responsible for the polarization of neutral atoms by the ions  $R_i^+$  and  $X_J^-$ . It is more convenient to determine the energy of polarization in the electrostatic approximation, separating it as

a special term  $\epsilon_i$ ,<sup>41</sup>

$$H_{im,im} = \bar{H}_{im,im} + \epsilon_i. \quad (11)$$

Considering atoms and ions as non-overlapping spheres, one obtains

$$\epsilon_i = - \sum_j^{J-1} C_j \left( \frac{\vec{R}_{ij}}{R_{ij}^3} - \frac{\vec{R}_{ji}}{R_{ji}^3} \right)^2 + \Delta_i, \quad j \neq i, \quad (12)$$

$$C_j = e^2 \alpha_j / 2, \quad (13)$$

where  $\alpha_j$  are the rare gas atom polarizabilities,  $\vec{R}_{ij}$  and  $\vec{R}_{ji}$  are the vectors between the corresponding atoms, and  $\Delta_i$  includes the dipole-dipole interaction. The matrix elements  $\bar{H}_{im,im}$  are obtained by using the Hamiltonian without polarization terms  $-C_j/R_{ij}^4$ :

$$\begin{aligned} \bar{H} = & \sum_j^{J-1} \bar{h}_j(v_j) + \sum_{j_1}^{J-2} \sum_{j_2(>j_1)}^{J-1} h_{j_1 j_2}(v_{j_1} + v_{j_2}) + \bar{h}_i(v_i - 1) + \sum_j^{J-1} \bar{h}_{ij}(v_i - 1 + v_j) + \\ & \bar{h}_j(v_j + 1) + \sum_j^{J-1} \bar{h}_{jJ}(v_j + v_J + 1) + h_{iJ}(v_i + v_J), \end{aligned} \quad (10')$$

$$\bar{h}_{ij} = h_{ij} - (-C_j/R_{ij}^4) \quad (14)$$

Using the expressions (3), (6) and (10'), one obtains

$$\begin{aligned} \bar{H}_{im,im} = \int dv \phi_{im} \bar{H} \phi_{im} = I_i - A_J + \sum_{j_1}^{J-2} \sum_{j_2(>j_1)}^{J-1} U_{j_1 j_2}^{(00)} + \\ \sum_j^{J-1} (U_{im,j}^{(+0)} + U_{J,j}^{(-0)}) + U_{im,J}^{(+-)}, \quad j_1 j_2 \neq i, \end{aligned} \quad (15)$$

$$U_{im,j}^{(+0)} = \int dv [\chi_{im}^{(+)}]^2 \bar{h}_{ij} [\chi_j^{(0)}]^2 = U_{im,j}^{(+0)} + C_j/R_{ij}^4, \quad i=1,2..J-1, j \neq i. \quad (16)$$

The off-diagonal matrix elements between the ionic states with the same localization of the positive charge but different orientation  $m$  are obtained

in the same way as the matrix elements in Eq.(9),

$$H_{im_1, im_2} = \int dv \phi_{im_1} \hat{H} \phi_{im_2} = \sum_j^{J-1} \int dv [x_j^{(0)}]^2 \bar{h}_{ij} x_{im_1}^{(+)} x_{im_2}^{(+)} + \int dv [x_j^{(-)}]^2 \bar{h}_{ij} x_{im_1}^{(+)} x_{im_2}^{(+)}, \quad j \neq i. \quad (17)$$

The off-diagonal matrix elements between the ionic states with different localization of the positive charge and between the neutral and ionic states are also obtained in a similar way,

$$H_{i_1 m_1, i_2 m_2} = \int dv x_{i_1}^{(0)} x_{i_2 m_2}^{(+)} \hat{H}_{i_1 i_2} (v_{i_1} + v_{i_2} - 1) x_{i_1 m_1}^{(+)} x_{i_2}^{(0)}, \quad (18)$$

$$H_{J m_1, im_2} = \int dv x_{J m_1}^{(0)} x_i^{(0)} \hat{H}_{J i} (v_i + v_J) x_J^{(-)} x_{im_2}^{(+)}, \quad (19)$$

where  $\hat{H}_{i_1 i_2} (v_{i_1} + v_{i_2} - 1)$  is the Hamiltonian of the charged  $(R_{i_1} R_{i_2})^+$  diatomic fragment and  $\hat{H}_{J i} (v_i + v_J)$  is the Hamiltonian of the  $R_i X_J$  diatomic fragment. The exchange integral (18) presents the valence interaction between two rare gas atoms with a common +1 charge. The exchange integral (19) is responsible for the coupling between the neutral and ionic states of the rare gas-halogen diatomic systems.

The matrix elements obtained above are expressed by diatomic terms which are determined by atomic group functions oriented, when of P symmetry, along Cartesian (x,y,z) axes. In order to express the matrix elements by the diatomic terms of usual  $\Sigma$  and  $\Pi$  orientations, one needs to transform the P symmetrical group functions to a new set of functions

$$x_{im} = \sum_{k=1}^3 S_{ij, mk} \psi_{ik, j}, \quad (20)$$

where the indices  $m=1,2,3$  indicate the x-, y- and z-orientations, respectively,  $\psi_{i1, j}$  is the  $\Sigma$  group function of the i-th atom oriented along

the  $\vec{R}_{ij}$  vector connecting the two atoms, and  $\psi_{i2,j}$  and  $\psi_{i3,j}$  are the group functions of the  $i$ -th atom oriented perpendicular to the  $\vec{R}_{ij}$ -vector. We will choose one of these two perpendicular orientations ( $\Pi$ ) as located in the plane formed by the  $\vec{R}_{ij}$ -vector and the  $x$ -axis. The second orientation which is perpendicular to this plane will be denoted by  $\bar{\Pi}$ . The  $3 \times 3$   $S_{ij,mk}$ -matrix has the form

$$\begin{aligned} S_{ij,11} &\equiv S_{ij,x\Sigma} = (x_j - x_i)/R_{ij}, & S_{ij,12} &\equiv S_{ij,x\Pi} = r_{ij}/R_{ij}, \\ S_{ij,13} &\equiv S_{ij,x\bar{\Pi}} = 0 \end{aligned} \quad (21)$$

$$\begin{aligned} S_{ij,21} &\equiv S_{ij,y\Sigma} = (y_j - y_i)/R_{ij}, & S_{ij,22} &\equiv S_{ij,y\Pi} = \\ &-(x_j - x_i)(y_j - y_i)/(R_{ij}r_{ij}), & S_{ij,23} &\equiv S_{ij,y\bar{\Pi}} = (z_j - z_i)/r_{ij} \end{aligned} \quad (21')$$

$$\begin{aligned} S_{ij,31} &\equiv S_{ij,z\Sigma} = (z_j - z_i)/R_{ij}, & S_{ij,32} &\equiv S_{ij,z\Pi} = \\ &-(x_j - x_i)(z_j - z_i)/(R_{ij}r_{ij}), & S_{ij,33} &\equiv S_{ij,z\bar{\Pi}} = -(y_j - y_i)/r_{ij}, \end{aligned} \quad (21'')$$

where  $R_{ij}$  is the interatomic distance and  $r_{ij}$  is the projection of the  $R_{ij}$  vector on the  $yz$ -plane,

$$R_{ij} = \sqrt{(x_j - x_i)^2 + (y_j - y_i)^2 + (z_j - z_i)^2} \quad (22)$$

$$r_{ij} = \sqrt{(y_j - y_i)^2 + (z_j - z_i)^2}. \quad (22')$$

Using the transformation (21) we will express the matrix elements (7), (9), (15), (17), (18) and (19) by  $\Sigma$  and  $\Pi$  diatomic terms,

$$\begin{aligned} H_{Jm,Jm} &= \sum_{j_1}^{J-2} \sum_{j_2(>j_1)}^{J-1} U_{j_1,j_2}^{(00)} + \sum_j^{J-1} [S_{Jj,m\Sigma}^2 U_{Jj,\Sigma}^{(00)} \\ &+ (S_{Jj,m\Pi}^2 + S_{Jj,m\bar{\Pi}}^2) U_{Jj,\Pi}^{(00)}] \end{aligned} \quad (23)$$



$$\begin{aligned}
H_{im,im} = & I_i - A_J + \sum_{j_1}^{J-2} \sum_{j_2(>j_1)}^{J-1} U_{j_1,j_2}^{(00)} + \sum_j^{J-1} [S_{ij,m\Sigma}^2 U_{ij,\Sigma}^{(+0)} \\
& + (S_{ij,m\Pi}^2 + S_{ij,m\bar{\Pi}}^2) U_{ij,\Pi}^{(+0)}] + S_{iJ,m\Sigma}^2 U_{iJ,\Sigma}^{(+0)} \\
& + (S_{iJ,m\Pi}^2 + S_{iJ,m\bar{\Pi}}^2) U_{iJ,\Pi}^{(+0)} + \sum_j^{J-1} U_{jJ}^{(0-)} + \epsilon_i, \quad j, j_1, j_2 \neq i \quad (24)
\end{aligned}$$

$$\begin{aligned}
H_{Jm_1,Jm_2} = & \sum_j^{J-1} [S_{Jj,m_1\Sigma} S_{Jj,m_2\Sigma} U_{Jj,\Sigma}^{(00)} \\
& + (S_{Jj,m_1\Pi} S_{Jj,m_2\Pi} + S_{Jj,m_1\bar{\Pi}} S_{Jj,m_2\bar{\Pi}}) U_{Jj,\Pi}^{(00)}], \quad (25)
\end{aligned}$$

$$\begin{aligned}
H_{im_1,im_2} = & \sum_j^{J-1} [S_{ij,m_1\Sigma} S_{ij,m_2\Sigma} U_{ij,\Sigma}^{(+0)} + (S_{ij,m_1\Pi} S_{ij,m_2\Pi} \\
& + S_{ij,m_1\bar{\Pi}} S_{ij,m_2\bar{\Pi}}) U_{ij,\Pi}^{(+0)}] + S_{iJ,m_1\Sigma} S_{iJ,m_2\Sigma} U_{iJ,\Sigma}^{(+0)} + (S_{iJ,m_1\Pi} S_{iJ,m_2\Pi} \\
& + S_{iJ,m_1\bar{\Pi}} S_{iJ,m_2\bar{\Pi}}) U_{iJ,\Pi}^{(+0)}, \quad j \neq i \quad (26)
\end{aligned}$$

$$\begin{aligned}
H_{i_1m_1,i_2m_2} = & S_{i_1i_2,m_1\Sigma} S_{i_2i_1,m_2\Sigma} V_{i_1i_2,\Sigma} + (S_{i_1i_2,m_1\Pi} S_{i_2i_1,m_2\Pi} + \\
& S_{i_1i_2,m_1\bar{\Pi}} S_{i_2i_1,m_2\bar{\Pi}}) V_{i_1i_2,\Pi} \quad (27)
\end{aligned}$$

$$\begin{aligned}
H_{Jm_1,im_2} = & S_{Ji,m_1\Sigma} S_{iJ,m_2\Sigma} V_{Ji,\Sigma} + (S_{Ji,m_1\Pi} S_{iJ,m_2\Pi} \\
& + S_{Ji,m_1\bar{\Pi}} S_{iJ,m_2\bar{\Pi}}) V_{Ji,\Pi}. \quad (28)
\end{aligned}$$

The diatomic terms  $V_{i_1i_2}$  and  $V_{Ji}$  in the off-diagonal matrix elements (27) and (28) are expressed by the integrals (18) and (19), respectively, with the only difference that instead of x,y,z-oriented functions  $\chi$ , the  $\Sigma, \Pi$ -oriented functions  $\psi$  of Eq. (20) are used. The diatomic U terms in the matrix elements (23)-(26) will be called Coulombic or diabatic potentials as they do not include exchange interactions presented by the off-diagonal

matrix elements (27)-(28). We have to note that the Coulombic terms  $U$  can include in a semiempirical way the van der Waals interaction which is not of Coulombic character.

The  $3J \times 3J$  matrix  $H$  provides  $3J$  eigenvalues  $E_k$  and  $3J$  eigenvectors  $c_{im}^{(k)}$  of the wave function of Eq.(4). Using the eigenvectors  $c_{im}^{(k)}$ , it is possible to calculate both static and transition moments. In the ZOA0 approximation the static dipole moment of any state is completely determined by the contribution of the ionic configuration. The x-component of the dipole moment  $\vec{\mu}_k$  is

$$(\vec{\mu}_k)_x = e \sum_{i=1}^{J-1} w_i^{(k)} (\vec{R}_J - \vec{R}_i)_x \quad (29)$$

$$w_i^{(k)} = \sum_m (c_{im}^{(k)})^2, \quad (30)$$

where  $e$  is the electron charge and  $\vec{R}_J$  and  $\vec{R}_i$  are the radius vectors of the ions. The transition moment between a state with largely ionic configuration and a state with largely neutral configuration is

$$(\vec{\mu}_{kl})_x = e \sum_{i=1}^{J-1} w_i^{(kl)} (\vec{R}_J - \vec{R}_i)_x \quad (31)$$

$$w_i^{(kl)} = \sum_m c_{im}^{(k)} c_{im}^{(l)}. \quad (32)$$

### III. Diatomic Coulombic and exchange terms

In the previous section the matrix elements of a polyatomic system were expressed by diatomic Coulombic ( $U$ ) and exchange ( $V$ ) terms. We shall now express these Coulombic and exchange terms by diatomic potentials which are assumed to be known. For the sake of simplicity, our study will be

restricted to systems with identical rare gas atoms  $R_i$ . There are four kinds of diatomic fragments:  $R_2$ ,  $R_2^+$ ,  $RX^-$  and  $RX$ . The expressions for the energy of any diatomic fragment will be obtained from the matrix elements of the previous section by removing all atoms to infinity except those which belong to this fragment.

#### A. R-R interaction

In the case of the  $R_i R_j$  diatomic fragment, the ground state energy is equal to the diagonal matrix element [Eq.(23)] with one non-zero term only, namely  $U_{ij}^{(00)}$ . It follows that the diatomic term  $U_{ij}^{(00)}$  is identical to the  $R_2$  ground-state  $\Sigma$  potential

$$U_{ij}^{(00)} = \Sigma. \quad (33)$$

#### B. $(R-R)^+$ interaction

The energy of the diatomic fragment  $(R_i R_j)^+$  is determined by a  $2 \times 2$  matrix with non-zero off-diagonal matrix elements. In the case of the  $\Sigma$ -oriented  $R^+$  wave function, the diagonal matrix element (24) and the off-diagonal matrix element (27) become

$$H_{11} = H_{22} = I_R - A_X + U_{ij,\Sigma}^{(+0)} - C_4/R_{ij}^4 = I_R - A_X + U_{ij,\Sigma}^{(+0)} \quad (34)$$

$$H_{12} = V_{ij,\Sigma}, \quad (34')$$

where  $-C_4/R_{ij}^4$  is the polarization energy  $\epsilon$ . The matrix elements (34) and (34') provide a ground-state potential  $\Sigma_g$  and an excited state potential  $\Sigma_u$ . Considering these potentials relative to the energy of separated ion  $R^+$  and neutral atom  $R$ , one obtains

$$U_{ij,\Sigma}^{(+0)} = \frac{1}{2}(\Sigma_u + \Sigma_g), \quad U_{ij,\Sigma}^{(+0)} = U_{ij,\Sigma}^{(+0)} + C_4/R_{ij}^4 \quad (35)$$

$$V_{ij,\Sigma} = \frac{1}{2}(\Sigma_u - \Sigma_g). \quad (36)$$

Similar expressions are valid also for the  $\Pi$  states, with the only

difference that the lower state is  $\pi_u$  whereas the higher state is  $\pi_g$ ,

$$U_{ij,\pi}^{(+0)} = \frac{1}{2}(\pi_g + \pi_u), \quad U_{ij,\pi}^{(+0)} = U_{ij,\pi}^{(+0)} + C_4/R_{ij}^4 \quad (37)$$

$$V_{ij,\pi} = \frac{1}{2}(\pi_g - \pi_u). \quad (38)$$

### C. $R-X^-$ interaction

In the case of the  $R_1X_J^-$  diatomic fragment the ground state energy is equal to the diagonal matrix element (24) with one non-zero diatomic term  $U_{iJ}^{(0-)}$  along with the difference  $I_R - A_X$  and the polarization energy term  $\epsilon$  equal to  $-C_4/R_{iJ}^4$ . Denoting by  $\Sigma$  the  $RX^-$  ground state potential determined relatively to the separated R atom and  $X^-$  ion one obtains

$$U_{iJ}^{(0-)} = \Sigma, \quad U_{iJ}^{(0-)} = \Sigma + C_4/R_{iJ}^4 \quad (39)$$

### D. $R-X$ interaction

Because of the ionic-neutral coupling, the  $R-X$  diatomic potentials are not connected explicitly with the Coulomb terms  $U_{iJ}$ , like in the previous cases, but rather are obtained as the eigenvalues of a  $2 \times 2$  matrix with the diagonal elements expressed by the Coulombic terms  $U_{iJ}$  and the off-diagonal elements equal to the exchange term  $V_{iJ}$ . In the case of the  $\Sigma$ -orientation, the matrix elements, derived from Eqs. (23), (24) and (28), are

$$H_{11} = U_{iJ,\Sigma}^{(00)} \quad (40)$$

$$H_{22} = I_R - A_X + U_{iJ,\Sigma}^{(+)} \quad (40')$$

$$H_{12} = V_{iJ,\Sigma} \quad (40'')$$

The matrix (40) allows us to express the Coulombic terms  $U_{iJ,\Sigma}^{(00)}$  and  $U_{iJ,\Sigma}^{(+-)}$  in terms of its eigenvalues, i.e., the  $RX$  ground-state ( $1\Sigma$ ) and excited-state ( $2\Sigma$ ) potentials which are assumed to be known:

$$U_{\Sigma}^{(00)} = \frac{1}{2}(1\Sigma + 2\Sigma - \beta) \quad (41)$$

$$U_{\Sigma}^{(+)} = \frac{1}{2}(1\Sigma + 2\Sigma + \beta) - (I_R - A_X) \quad (42)$$

$$\beta = \sqrt{(2\Sigma - 1\Sigma)^2 - 4V_{\Sigma}^2} \quad (43)$$

Similar expressions are valid for the  $\Pi$ -oriented potentials  $U_{\Pi}^{(00)}$  and  $U_{\Pi}^{(+-)}$ .

Equations (41)-(42) exclude from the R-X potentials the ionic-neutral coupling term  $V_{iJ}$ , which must be found independently. Before estimating this term, we shall consider the influence of the ionic-neutral coupling on the R-X properties. Due to this coupling, the ground state ( $1\Sigma$ ) of the rare gas-halogen molecule is a mix of "pure" neutral and ionic states whose energies are determined by the diagonal matrix elements (40) and (40'). Because the ionization potential of the rare gas atom  $I_R$  is much higher than the electron affinity of the halogen atom  $A_X$ , the  $H_{22} - H_{11}$  difference is large. It results in relatively weak coupling, at least for distances exceeding the van der Waals equilibrium distance.<sup>20,22</sup> However, this coupling significantly affects some of the properties of the rare gas-halogen systems. These properties can be used to find the coupling terms by semiempirical fitting. In the present calculation the coupling term  $V_{iJ}$  is found by fitting the  $RX \rightarrow R^+X^-$  transition moment which depends strongly on  $V_{iJ}$  and vanishes when  $V_{iJ}$  is zero.

#### IV. Diatomic terms of the $Xe_nCl$ systems

For the  $Xe_nCl$  systems the diatomic fragments are:  $Xe-Xe$ ,  $(Xe-Xe)^+$ ,  $Xe-Cl^-$  and  $Xe-Cl$ . The Coulombic potentials and the exchange terms of all of these diatomic fragments, except  $Xe-Cl$ , are expressed by diatomic  $\Sigma$  or  $\Pi$  potentials [see Eqs. (33)-(39)]. In the case of the  $Xe-Cl$  diatomic fragment, as it was shown in the previous section, the Coulombic potentials  $U$  [Eqs. (41)-(42)] are expressed not only by diatomic potentials but also by the exchange (coupling) term  $V$ , which has to be found independently.

The diatomic potentials can be taken either from experimental studies or from ab initio calculations. In the present calculation, when possible, empirical potentials were used. The diatomic potentials were expressed analytically by the equation

$$U = U_0 + A \exp[-\alpha R] - C_6/R^6 - C_4/R^4 - C_1/R, \quad (44)$$

where  $R$  is the interatomic distance,  $U_0$  is the energy of two separated atoms or ions,  $C_6$  is the van der Waals coefficient,  $C_4$  is the polarization coefficient [Eq.(13)], and  $C_1 = e^2$  is the coefficient of the electrostatic attraction between two opposite charges. In the case of a pair of neutral atoms, only the repulsive and van der Waals terms remain since  $C_1 = C_4 = 0$ :

$$U = U_0 + A \exp[-\alpha R] - C_6/R^6 \quad (44')$$

The  $\bar{U}$  potential [Eq.(16)] of an ion-atom pair is also expressed by Eq. (44'), since  $C_1 = 0$  and the polarization term is excluded. For a better fitting, some of the potentials can include two exponential functions or the  $-C_8/R^8$  term. The exchange terms  $V$  are expressed by an exponential function

$$V = A \exp[-\alpha R]. \quad (45)$$

The parameters of Eqs. (44) and (45) are presented in Table 1. The sources of the potentials are given below.

#### A. Xe-Xe potential

The parameters of the expression (44') for the ground state  $\Sigma$  potential were obtained by the interpolation of the experimental data of the Xe-Xe interaction.<sup>42</sup>

#### B. (Xe-Xe)<sup>+</sup> potentials and exchange terms

The ab initio  $\text{Xe}_2^+$  potential curves  $\Sigma_g$ ,  $\Sigma_u$ ,  $\Pi_u$ ,  $\Pi_g$  without spin-orbit coupling<sup>43</sup> were used to calculate the Coulombic potentials  $U$  [Eqs.(35) and (37)] and the exchange terms  $V$  [Eqs. (36) and (38)]. These potentials are

preferable as they provide the ground-state potential well ( $D_e = 1.08\text{eV}$ ,  $R_e = 3.22 \text{ \AA}$ ) which is more reliable from the point of view of experimental results<sup>44</sup> than that obtained in Ref. 43 by including the spin-orbit coupling. The  $(\text{Xe-Xe})^+$  diatomic terms,  $U$  and  $V$ , were interpolated by the analytical expressions, Eqs.(44) and (45).

### C. Xe-Cl<sup>-</sup> potential

The Xe-Cl<sup>-</sup>  $\Sigma$  potential was obtained by interpolation of experimental data.<sup>45</sup> In order to obtain better fitting for short distances, the repulsive term is described by two exponential functions.

### D. Xe-Cl potentials and coupling terms (Fig. 1)

In order to find the Xe-Cl Coulombic terms  $U^{(00)}$  and  $U^{(+-)}$ , one needs the Xe-Cl potentials and the coupling term  $V$  [see the Eqs. (41)-(42)]. The potential curves of the ground state  $1\Sigma(X)$  and the excited ionic state  $2\Sigma(B)$  were obtained by the interpolation of experimental data.<sup>26</sup> The potential curve of the excited ionic  $2\Pi(C)$  state is similar to the  $2\Sigma(B)$  potential curve.<sup>22</sup> The equilibrium point energy of  $2\Pi$  was found experimentally to be almost the same as in the  $2\Sigma$  state<sup>46</sup> or to be lower by only  $0.016 \text{ eV}$ <sup>8</sup> or  $0.028 \text{ eV}$ .<sup>47</sup> The  $2\Pi$  equilibrium distance was found to be  $R_e = 3.074 \text{ \AA}$ ,<sup>47</sup> which is larger by  $-0.06 \text{ \AA}$  than that in the  $2\Sigma$  state. The  $2\Pi$  potential curve used in this paper has a minimum at the point  $R_e = 3.074 \text{ \AA}$  and minimum energy value lower than the  $2\Sigma$  state by  $0.02 \text{ eV}$ , which is a compromise of different experimental results.<sup>8,46,47</sup> The polarization coefficient  $C_4$  for the  $2\Pi$  potential is assumed to be the same as for the  $2\Sigma$  potential curve.

The potential curve of the first excited  $1\Pi(A)$  state was found to have a minimum at the point  $R_e = 4.1 \text{ \AA}$ .<sup>48</sup> The  $1\Pi$  potential curve used in the present paper fits this minimum point and the energy of transition from the

equilibrium point of the  $2\Pi$  state to the repulsive  $1\Pi$  state, which is equal to 3.59 eV (345 nm).<sup>49</sup>

By using empirical Xe-Cl potentials we take into account indirectly the spin-orbit coupling, but only as a shift of the diatomic terms in the diagonal matrix elements. Any influence of the interaction of the Xe-Cl fragment with other atoms on the spin-orbit coupling is neglected. Besides, the consideration is restricted to states which correspond asymptotically to the  $\text{Xe}^+$  and Cl atoms in their  $P_{3/2}$  state.

As mentioned in the previous section, the coupling terms  $V_\Sigma$  and  $V_\Pi$  which are responsible for the mixing of the neutral and ionic states can be considered as semiempirical parameters. In the present calculation they were determined by fitting the XeCl transition moments. The ab initio transition moments were found as functions of interatomic distances.<sup>22</sup> The empirical transition moments can be found at the equilibrium points of the ionic states by using the radiative lifetime  $\tau_{kl}$ ,<sup>22</sup>

$$\mu_{kl} = 77.9(E_k - E_l)^{-3/2} \sqrt{\tau_{kl}}, \quad E_k > E_l \quad (46)$$

where  $\mu$  is expressed in Debyes (D),  $E$  in eV, and  $\tau$  in nsec. The lifetimes of the B $\rightarrow$ X and C $\rightarrow$ A (Fig. 1) transitions are equal to 11.1 ns and 131 ns, respectively.<sup>49</sup> Substituting these values in the expression (46), as well as the energy differences (4.02 eV for B $\rightarrow$ X and 3.59 eV for C $\rightarrow$ A transition), one obtains  $\mu_\Sigma = 2.9$  D for the B $\rightarrow$ X transition moment and  $\mu_\Pi = 1.0$  D for the C $\rightarrow$ A transition moment. These values were fitted by the coupling terms  $V_\Sigma$  and  $V_\Pi$  presented as exponential functions [Eq.(45)]. The coefficients  $\alpha$  of these exponential functions were determined by using the ab initio transition moments.<sup>22</sup> The parameters of the coupling functions are given in



Table 1. The dependence of the B-X and C-A transition moments on the Xe-Cl distance is demonstrated in Fig. 2a.

The effect of the coupling on the Xe-Cl interaction is demonstrated in Fig. 2b by presenting the coupling energy, which is equal to the difference between the Coulombic potential  $U_{\Sigma}^{(00)}$  and the ground-state potential  $1\Sigma$ , and the contribution (in %) of the ionic  $\text{Xe}^+\text{Cl}^-$  configuration to the ground state. Both the coupling energy and the ionic configuration contribution decrease exponentially as the internuclear distance increases. At the point of the van der Waals equilibrium (3.23 Å), the coupling energy is 0.10 eV, almost equal to the energy of the van der Waals attraction (0.12 eV). The contribution of the ionic configuration at this point is 2.4%.

#### V. Results of calculations

The semiempirical DIIS calculations were performed for the following  $\text{Xe}_n\text{Cl}$  systems:  $\text{Xe}_2\text{Cl}$ ,  $\text{Xe}_3\text{Cl}$  and  $\text{Xe}_{12}\text{Cl}$ . The  $\text{Xe}_2\text{Cl}$  system has been studied both experimentally<sup>7,9,11,12</sup> and theoretically.<sup>28,30</sup> In the present calculation, which unlike another semiempirical calculation<sup>30</sup> takes into account directly the neutral-ionic coupling, the transition moments were obtained as well. The  $\text{Xe}_3\text{Cl}$  and  $\text{Xe}_{12}\text{Cl}$  systems are considered here in order to check the possibility of the formation of more stable ionic molecules than the  $\text{Xe}_2^+\text{Cl}^-$  molecule.

##### A. $\text{Xe}_2\text{Cl}$ system

According to the results of the present calculation, the quasistable  $\text{Xe}_2^+\text{Cl}^-$  molecule which is formed in the first ionic state  $4^2\Gamma$  has a configuration of an isosceles triangle, like in other  $\text{Xe}_2\text{Cl}$  calculations.<sup>28,30</sup> The Xe-Cl distance in the  $\text{Xe}_2^+\text{Cl}^-$  molecule is 3.23 Å, or 0.16 Å larger than in the diatomic  $\text{Xe}^+\text{Cl}^-$  molecule. The Xe-Xe distance (3.25 Å) only slightly exceeds the interatomic distance in the  $\text{Xe}_2^+$  molecule

(3.22 Å). The  $\text{Xe}_2\text{Cl}$  potential curves for a fixed Xe-Xe distance in the  $\text{Xe}_2^+\text{Cl}^-$  molecule (3.25 Å) are presented in Fig. 4a. The electronic states are denoted in the same way as in Ref. 30. Because of the neglect of the spin-orbit coupling, some of the states cannot be obtained in the present calculation. However, in contrast to Ref. 30, the calculation provides  $\Pi$  states with wave functions antisymmetric relatively to the molecule plane. The number of states is  $3 \times 3 = 9$ , including three largely neutral states and six largely ionic states. Three of these states ( $2^2\Gamma_\Pi$ ,  $4^2\Gamma_\Pi$ ,  $6^2\Gamma_\Pi$ ) are the states of  $\Pi$  symmetry. The potentials of the antisymmetric states  $4^2\Gamma_\Pi$  and  $6^2\Gamma_\Pi$  almost coincide with the  $5^2\Gamma$  and  $6^2\Gamma$  potentials of the symmetrical states. The  $\text{Xe}_2\text{Cl}$  potential curves for fixed Xe-Cl distance of the  $\text{Xe}_2^+\text{Cl}^-$  molecule (3.23 Å) are presented in Fig. 4a. The antisymmetric states  $2^2\Gamma_\Pi$ ,  $4^2\Gamma_\Pi$  and  $6^2\Gamma_\Pi$  and the highest state  $8^2\Gamma$  are not shown in Fig. 4a. The transition moments for the pairs of states  $1^2\Gamma-4^2\Gamma$ ,  $2^2\Gamma-4^2\Gamma$  and  $1^2\Gamma-5^2\Gamma$  are presented in Fig. 4b.

In the equilibrium configuration the energy of the  $\text{Xe}_2^+\text{Cl}^-$  molecule is 3.09 eV. The dominant transition from the  $4^2\Gamma$  state is to the ground state  $1^2\Gamma$  with the transition moment of 2.45 D, which is much higher than the ab initio transition moment of 0.96 D.<sup>28</sup> The transition moment to the state  $2^2\Gamma$  has a sharp minimum in the  $\text{Xe}_2^+\text{Cl}^-$  equilibrium geometry and is very small (Fig. 4b). The calculated energy of the  $4^2\Gamma-1^2\Gamma$  transition is 2.56 eV (485 nm), which is close to the experimental value of the center of the emission band (2.58 eV or 480 nm)<sup>11</sup> and to the ab initio value of 2.50 eV.<sup>28</sup> In the DIM calculation,<sup>30</sup> which was performed without taking into account directly the neutral-ionic coupling, the transition energy was found to be 2.74 eV. However, the difference between the transition energies in both calculations cannot be explained completely by the influence of the neutral-ionic

coupling, since in the DIM calculation<sup>30</sup> the ab initio diatomic potentials were used whereas the present study applies different, mainly empirical, diatomic potentials.

In order to check the influence of the coupling term  $V_{\Sigma}$  [see Eqs. (41)-(43)] on the results of calculation, the  $\text{Xe}_2^+\text{Cl}^-$  molecule was calculated also without the coupling term ( $V_{\Sigma} = 0$ ). By putting  $V_{\Sigma} = 0$  one does not neglect the neutral-ionic coupling since the empirical Xe-Cl diatomic potentials include it, but rather neglects only the dependence of the coupling energy on the system structure. The calculation shows that the neglect of the coupling term  $V_{\Sigma}$  decreases the energy of the excited ionic state by 0.07 eV, increases the energy of the ground state by 0.10 eV and, consequently, decreases the transition energy by 0.17 eV, which becomes equal to 2.38 eV. These energy changes demonstrate that the influence of the coupling term on the  $\text{Xe}_2\text{Cl}$  system does not change significantly the structure of the  $\text{Xe}_2\text{Cl}$  electronic states. Such relatively moderate influence of the coupling term on the  $\text{Xe}_2\text{Cl}$  can be explained by the fact that the mixing of neutral and ionic states in the  $\text{Xe}_2\text{Cl}$  system, as well as in other  $\text{Xe}_n\text{Cl}$  systems, does not differ much from that of the  $\text{XeCl}$  diatomic system. For example, the electronic structure of the  $\text{Xe}_2^+\text{Cl}^-$  molecule includes 3.6% of the neutral electronic configuration, or 1.8% for one  $\text{XeCl}$  fragment. The corresponding value for the  $\text{XeCl}$  system with the same interatomic distance (3.23 Å) is 2.3% (Fig. 2b).

In addition to the "main"  $4^2\Gamma \text{Xe}_2^+\text{Cl}^-$  molecule, there is also the quasistable collinear  $\text{XeClXe}$  molecule, which has  $\Sigma$  state symmetry and is 100% ionic. The Xe-Cl distances in this molecule are relatively short, 3.06 Å only. The  $\Sigma$  state molecule has 0.72 eV higher energy than the  $4^2\Gamma \text{Xe}_2^+\text{Cl}^-$  molecule and is separated from  $4^2\Gamma \text{Xe}_2^+\text{Cl}^-$  molecule by a high barrier. The

energy of transition to the ground state is 3.87 eV, and the transition moment is 3.9 D.

A quasistable molecule was found also in the ionic  $4^2\Gamma_{\Pi}$  state. Like in the  $4^2\Gamma$  state, the  $4^2\Gamma_{\Pi}$  ionic molecule has a configuration of an isosceles triangle. The Xe-Cl distances are even shorter in this molecule (3.13 Å). However, the Xe-Cl-Xe angle is much larger ( $85^\circ$ ), and consequently the Xe-Xe distance (4.23 Å) significantly exceeds the  $\text{Xe}_2^+$  equilibrium distance (3.22 Å). The energy of the  $4^2\Gamma_{\Pi} \text{Xe}_2^+\text{Cl}^-$  molecule is 0.8 eV higher than that of the  $4^2\Gamma \text{Xe}_2^+\text{Cl}^-$  molecule.

The ground state-potential energy surface is found to have two different van der Waals complexes with almost the same dissociation energy. One of these complexes, with the dissociation energy of 0.076 eV, has a symmetric XeClXe collinear configuration. The Xe-Cl distances are equal to 3.24 Å, which is 0.01 Å larger than in the XeCl diatomic complex. This slight increase in the Xe-Cl distance followed by an increase of the dissociation energy of 0.006 eV compared to the dissociation energy of two XeCl diatomic complexes can be explained only by the influence of the neutral-ionic coupling. The second van der Waals complex in the ground state, with the dissociation energy of 0.075 eV, has an asymmetric geometry. The Xe-Cl distances are 3.23 Å and 4.06 Å, and the Xe-Cl-Xe angle is equal to  $74.4^\circ$ . The energies of the excitation of the van der Waals symmetric (collinear) and asymmetric complexes to the ionic  $4^2\Gamma$  state are equal to 3.96 eV and 3.94 eV, respectively, compared to the excitation energy of 4.05 eV for the case of the XeCl diatomic complex. The  $1^2\Gamma \rightarrow 4^2\Gamma$  transition moment is large in the case of the collinear complex (3.32 D) but small (only 0.71 D) for the case of the asymmetric complex.

A van der Waals complex was found also in the first excited state ( $2^2\Gamma$ ). It has a symmetrical geometry with the Xe-Cl distance of 3.99 Å and the Xe-Cl-Xe angle of 68.4°. The dissociation energy of this complex is positive, 0.055 eV.

The equilibrium configurations in the neutral states were presented above as van der Waals complexes. However, this term is not precise here as the attractive forces are provided also by the neutral-ionic coupling.

#### B. Xe<sub>3</sub>Cl<sup>-</sup> system

In order to check the possibility of the attachment of more Xe atoms to the Xe<sub>2</sub><sup>+</sup>Cl<sup>-</sup> quasistable molecule, the Xe<sub>3</sub><sup>+</sup>Cl<sup>-</sup> system was studied. The formation of the Xe<sub>3</sub><sup>+</sup>Cl<sup>-</sup> molecules can be expected so far as the Xe<sub>3</sub><sup>+</sup> molecules were found experimentally.<sup>50</sup> The most stable Xe<sub>3</sub><sup>+</sup> configuration is a symmetric collinear one.<sup>51</sup> According to the results of our calculation, the Xe<sub>3</sub><sup>+</sup> arrangement in the Xe<sub>3</sub><sup>+</sup>Cl<sup>-</sup> molecule is not collinear. In the most stable configuration, the Cl atom and two Xe atoms form an isosceles triangle with the Xe-Cl distance of 3.24 Å and the Xe-Xe distance of 3.25 Å, which almost coincide with the interatomic distances in the  $4^2\Gamma$  Xe<sub>2</sub><sup>+</sup>Cl<sup>-</sup> molecule. The third Xe atom is located in the plane perpendicular to the triangle plane at a distance of 3.52 Å from the Cl atom and 4.41 Å from the two other Xe atoms. The energy of dissociation of the Xe<sub>3</sub><sup>+</sup>Cl<sup>-</sup> molecule to Xe<sub>2</sub><sup>+</sup>Cl<sup>-</sup> and Xe is positive, 0.113 eV. It follows that the Xe<sub>3</sub><sup>+</sup>Cl<sup>-</sup> can be formed, although the Xe<sub>2</sub><sup>+</sup>Cl<sup>-</sup>-Xe binding is weak and is determined mainly by the polarization interaction. The third Xe atom bears only 0.5% of the positive charge. The transition energy to the ground state is 2.48 eV. This value is not far from the Xe<sub>2</sub><sup>+</sup>Cl<sup>-</sup> transition energy (2.56 eV), which makes it difficult to distinguish the Xe<sub>3</sub><sup>+</sup>Cl<sup>-</sup> and Xe<sub>2</sub><sup>+</sup>Cl<sup>-</sup> molecules by their emission.

A less stable  $\text{Xe}_3^+\text{Cl}^-$  molecule is formed in the symmetric configuration with the Xe-Cl distance of 3.33 Å and Xe-Xe distance of 3.58 Å. The dissociation energy in this configuration is 0.08 eV, and the transition energy is 2.62 eV.

### C. $\text{Xe}_{12}^+\text{Cl}^-$ system

According to the results of the calculation, the spherical symmetric  $\text{Xe}_{12}^+\text{Cl}^-$  system is unstable. The stable configuration is formed by a  $\text{Xe}_2^+\text{Cl}^-$  molecule with slightly extended interatomic distances (3.29 Å for Xe-Cl and the same for Xe-Xe) and 10 weakly bounded Xe atoms. These 10 Xe atoms bear together only 4.3% of the positive charge. The energy of the dissociation of this system to  $\text{Xe}_2^+\text{Cl}^-$  and 10 Xe atoms is 0.88 eV. The energy of transition to the ground state is 2.49 eV. Considering the dissociation energies of the  $\text{Xe}_3\text{Cl}$  and  $\text{Xe}_{12}\text{Cl}$  systems, we have to note that they may be overestimated because of the neglect of three- and four-center interactions.<sup>52</sup>

## VI. Conclusion

1. The diatomic-in-ionic-systems (DIIS) method is designed for a semiempirical calculation of neutral polyatomic systems  $\text{R}_n\text{X}$ , which consist of atoms R of S symmetry and an atom X of P symmetry and which can form excited ionic  $\text{R}_n^+\text{X}^-$  states with positive ions  $\text{R}^+$  of P symmetry and a negative ion  $\text{X}^-$  of S symmetry. Rare gas(R)-halogen(X) systems satisfy this definition and have been subject of consideration in the present paper. The DIIS method can be also used, with some modifications in the matrix element expressions, for calculations of other systems, such as hydrogen-containing rare gas-halides  $\text{R}_n\text{H}_m\text{X}$ , alkali metal-halides and rare gas cluster ions  $\text{R}_n^+$ .

2. The DIIS method allows us to calculate the electronic structure of polyatomic systems by using diatomic potentials and transition moments as

initial data. In order to improve the results, it is possible also to use some known polyatomic values as semiempirical parameters. However the present calculation of polyatomic systems is based on diatomic data only. The calculation is limited to states without spin-orbit coupling. The influence of this coupling on the system energy is taken into account approximately and indirectly by using empirical diatomic potentials.

3. The DIIS method has been applied to the  $\text{Xe}_n\text{Cl}$  systems,  $\text{Xe}_2\text{Cl}$  in particular. The ionic  $\text{Xe}_2^+\text{Cl}^-$  in its most stable state ( $4^2\Gamma$ ) was found to have an equilibrium geometry of an isosceles triangle, like in other calculations.<sup>28,30</sup> In the equilibrium configuration the dominant transition is to the ground state, although in other configurations the radiative transition to the first excited state becomes possible as well. In addition to the  $4^2\Gamma$   $\text{Xe}_2^+\text{Cl}^-$  molecule, there are other quasistable ionic molecules with higher energy, in particular, the collinear  $\text{Xe}^{1/2+}\text{Cl}^-\text{Xe}^{1/2+}$  molecule. Any empirical evidence of the emission of these ionic molecules are unknown to us. In the ground state, two van der Waals complexes were found with the same dissociation energy but different geometries and different transition moments to the ionic states.

4. According to the results of the calculation, the ionic  $\text{Xe}_2^+\text{Cl}^-$  molecule attracts more Xe atoms, but without sharing with them much of the  $\text{Xe}_2^+$  positive charge. The ionic molecules with more than two Xe atoms,  $\text{Xe}_3^+\text{Cl}^-$  in particular, can be formed in a dense gas. It is difficult to detect these molecules as their emission wavelength is similar to that of the  $\text{Xe}_2^+\text{Cl}^-$  molecule.

5. The symmetric  $\text{Xe}_{12}^+\text{Cl}^-$  clusters were found to be unstable, so that their formation in rare gas solids<sup>13,20</sup> is unlikely.

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Table 1

Parameters of diatomic terms. For the designation of the parameters see Eqs. (44) and (45).  $R_e$  and  $D_e$  are the equilibrium distance and the dissociation energy, respectively.

		$U_0$	$\alpha$	$A$	$C_6$	$C_4$	$C_1$	$R_e$	$D_e$
diatomic									
fragment	term	eV	$\text{\AA}^{-1}$	eV	eV $\text{\AA}^6$	eV $\text{\AA}^4$	eV $\text{\AA}$	$\text{\AA}$	eV
Xe-Xe	$\Sigma$	0	3.17	24170	320	0	0	4.47	0.023
$\text{Xe}^+-\text{Xe}$	$U_\Sigma$	0	2.95	14520	320	29.14	0		
								3.22*	1.08*
$(\text{Xe}-\text{Xe})^+$	$V_\Sigma$	-	1.45	-172	-	-			
$\text{Xe}^+-\text{Xe}$	$U_\Pi$	0	3.00	18625	320	29.14	0		
								4.00*	0.16*
$(\text{Xe}-\text{Xe})^+$	$V_\Pi$	0	1.90	-168	-	-			
$\text{XeCl}^-$	$\Sigma$	0	3.85	31670	60	29.14	0	3.30	0.195
			8.0**	4.10 <sup>8</sup>					
Xe-Cl	$1\Sigma$	0	3.10	1167	99.2	0	0	3.23	0.035
$\text{Xe}^+-\text{Cl}^-$	$2\Sigma$	8.52	2.512	2033	0	66	14.4	3.01	453
Xe-Cl	$1\Pi$	0	3.90	86000	.2	0	0	4.10	0.015
					310***				
$\text{Xe}^+-\text{Cl}^-$	$2\Pi$	8.52	2.847	5520	0	66	14.4	3.074	3.97
Xe-Cl	$V_\Sigma$	-	1.20	-30	-	-	-	-	-
Xe-Cl	$V_\Pi$	-	1.40	-18	-	-	-	-	-

\*  $R_e$  and  $D_e$  for  $\text{Xe}_2^+$  potential curves connected with U and V by Eqs. (35)-(38).

\*\* Parameters of the second exponent of the  $\text{XeCl}^-$  potential.

\*\*\* Coefficient  $C_8$  of the  $C_8/R^8$  term of the  $1\Pi$  potential.

### Figure Captions

Fig. 1. XeCl potential curves (Table 1).

Fig. 2. The effects of coupling between ionic and neutral electronic configurations in the XeCl system. The vertical dashes stand for the  $2\Pi$  (C) equilibrium distance.

a) Stabilization energy of the coupling (right ordinate) and the contribution of ionic configuration (left ordinate) in the ground  $1\Sigma$  (X) state.

b)  $1\Sigma-2\Sigma$  (X-C) and  $1\Pi-2\Pi$  (A-C) transition moments.

Fig. 3.  $\text{Xe}_2\text{Cl}$  potential energy surfaces for a geometry (shown in the figure) with a fixed Xe-Xe distance equal to that of the  $\text{Xe}_2^+\text{Cl}^-$  ( $4^2\Gamma$  state) molecule. The vertical dashes stand for the equilibrium  $\text{Xe}_2^+\text{Cl}^-$  configuration.

Fig. 4.  $\text{Xe}_2\text{Cl}$  system in a geometry (shown in the figure) with a fixed Xe-Cl distance equal to that of the  $\text{Xe}_2^+\text{Cl}^-$  ( $4^2\Gamma$  state) molecule. The vertical dashes stand for the equilibrium  $\text{Xe}_2^+\text{Cl}^-$  configuration.

a) potential energy surfaces for five  $^2\Gamma$  states.

b)  $1^2\Gamma-4^2\Gamma$ ,  $1^2\Gamma-5^2\Gamma$  and  $2^2\Gamma-4^2\Gamma$  transition moments.

Fig. 1

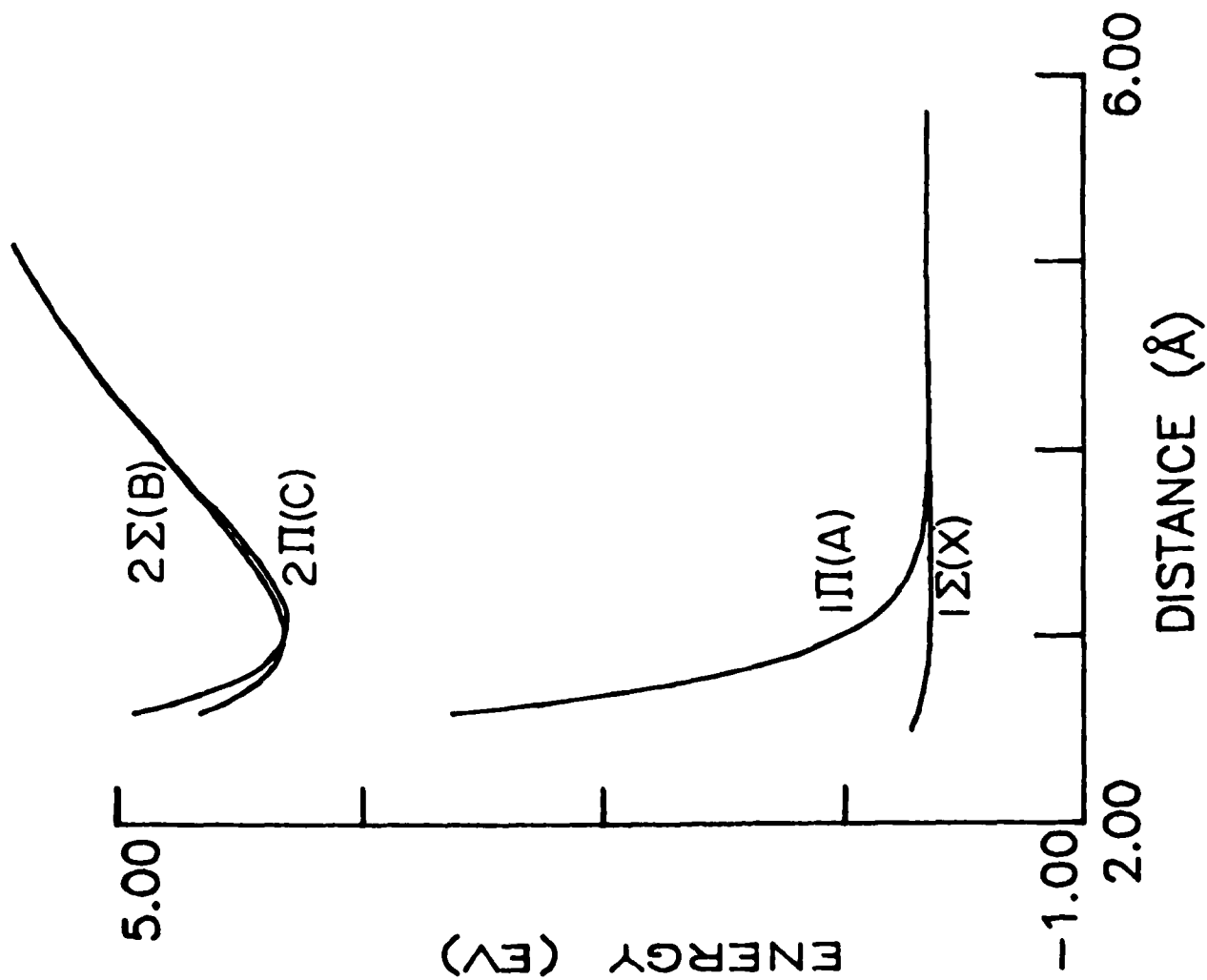


Fig. 2(a)

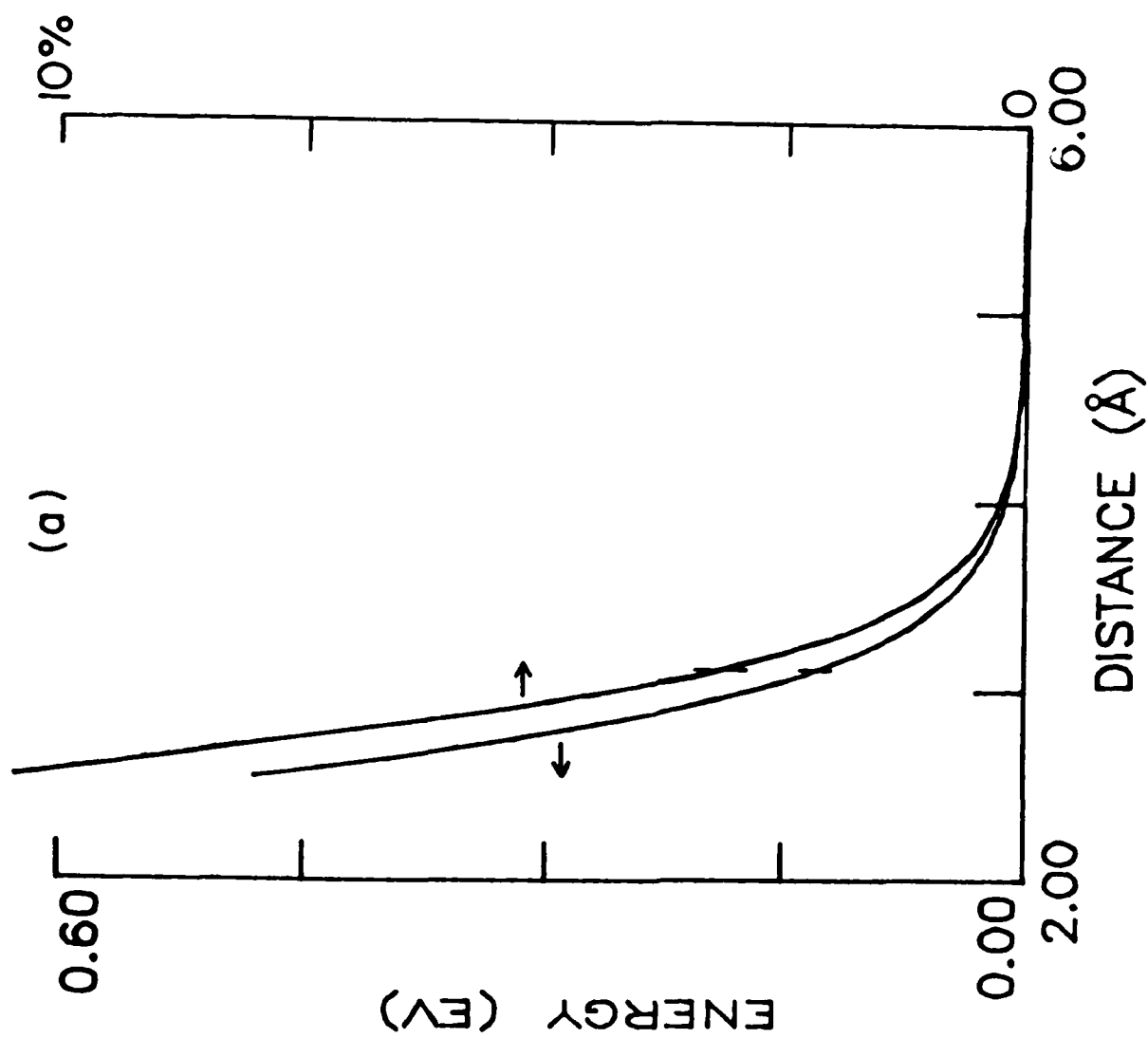


Fig. 2(b)

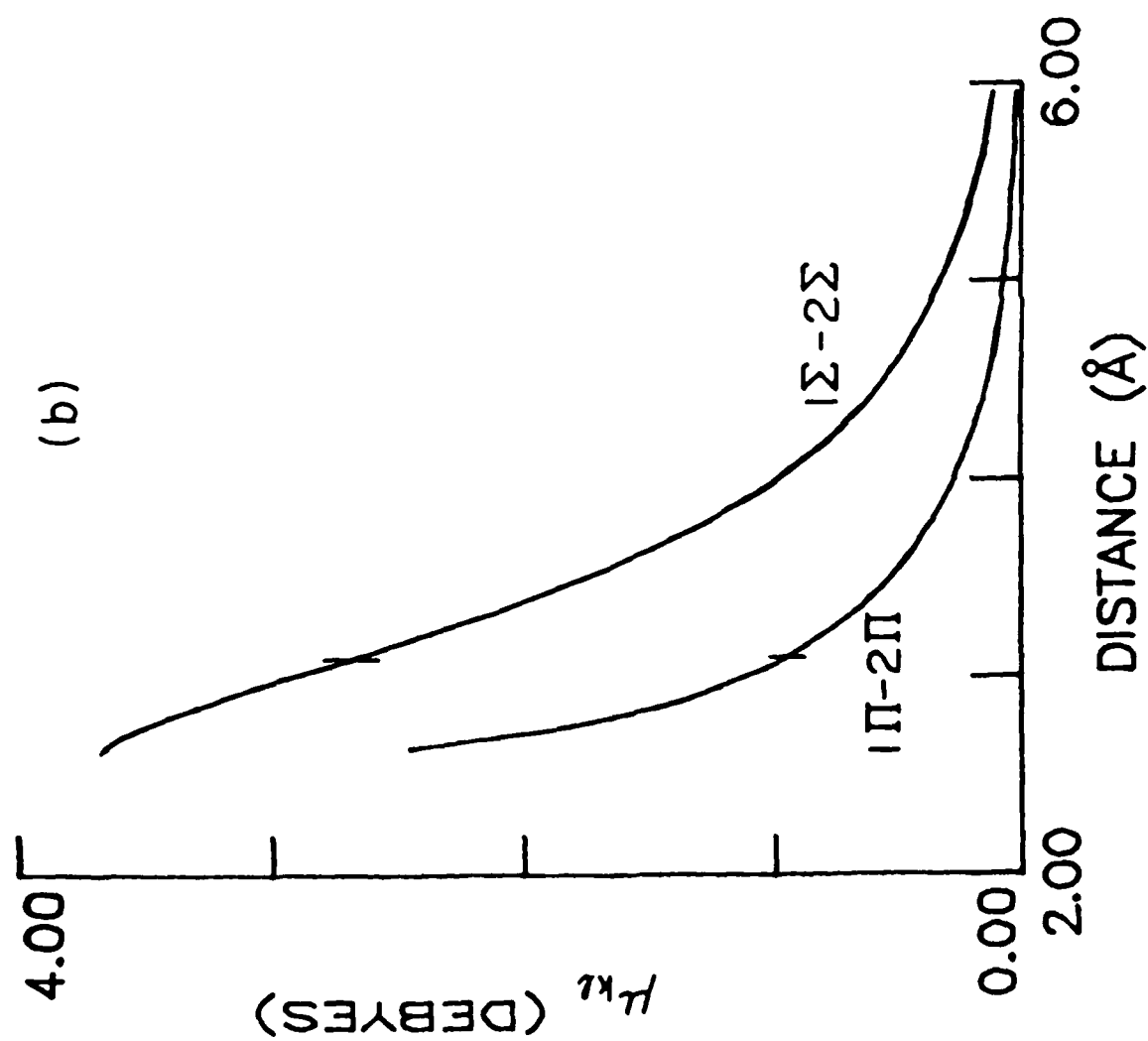
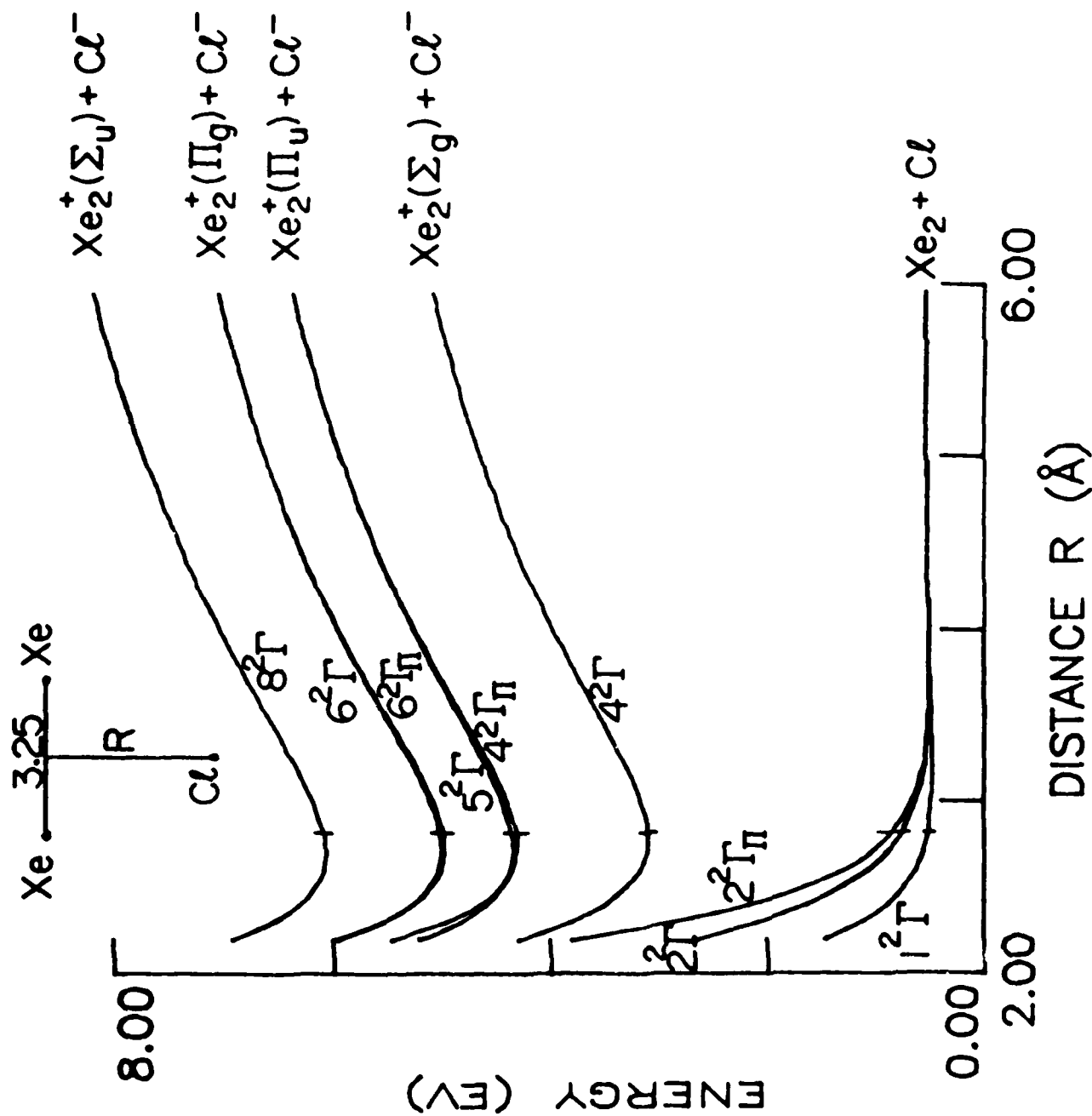




Fig. 3



(a)

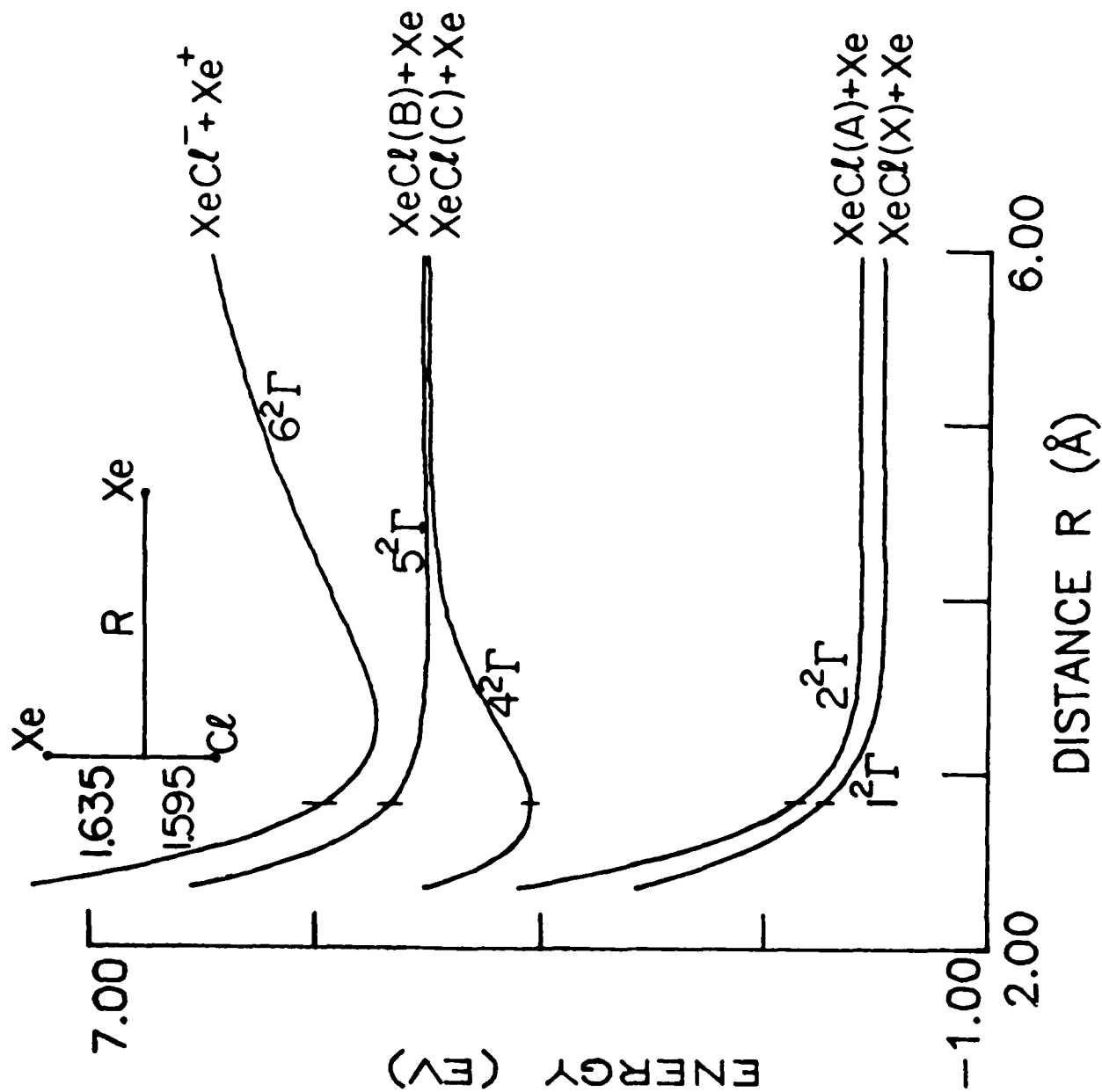
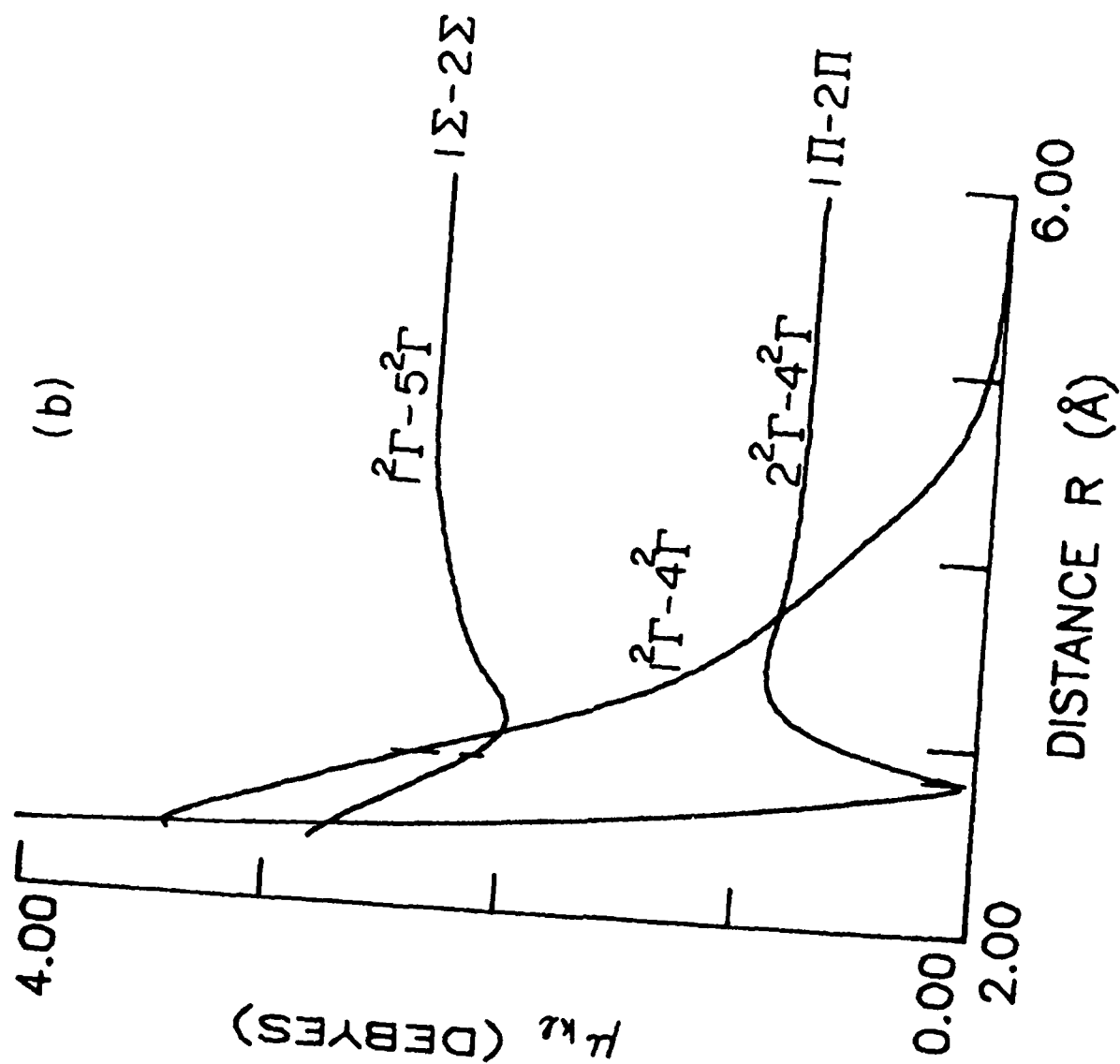


Fig. 4 (b)



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